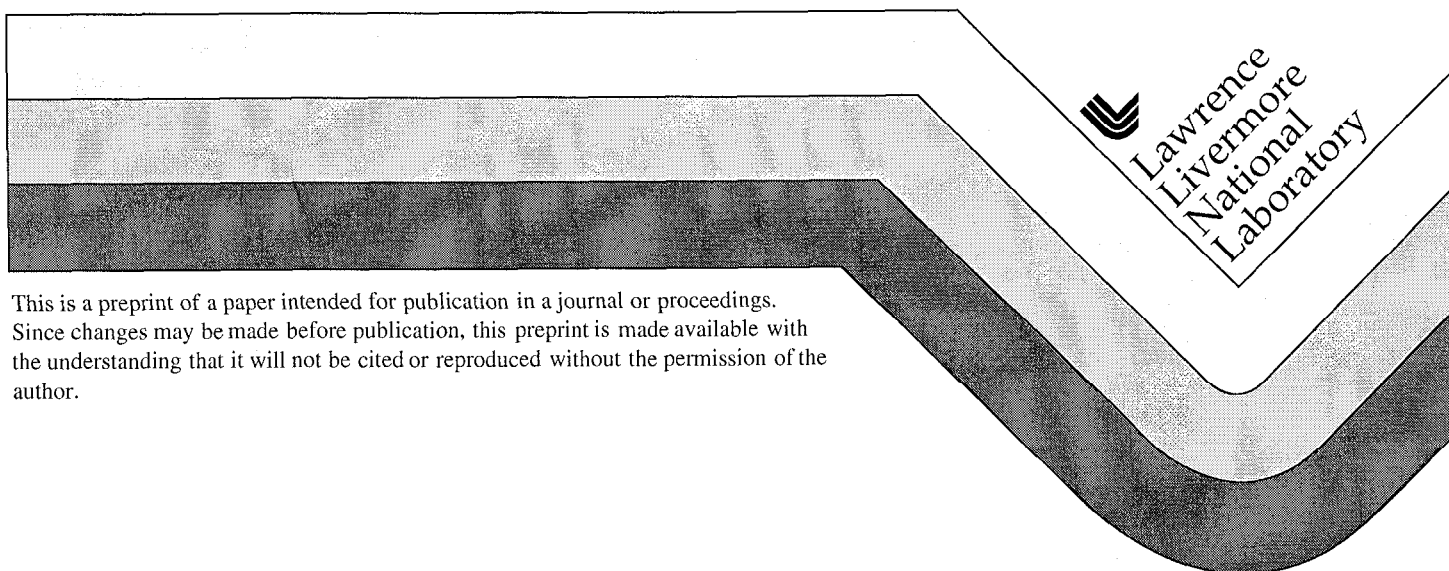


Comparison of Commercial UV Lamps for Radical Oxidation and Direct Photolysis in Water

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***Comparison of Commercial UV Lamps for Radical Oxidation and Direct Photolysis in Water**

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INTRODUCTION

Lawrence Livermore National Laboratory (LLNL) is charged with developing methods for treating contaminated sites and destroying waste organic compounds that are currently being accumulated, including Trimsol (machining oil), trichloroethene (TCE), tributyl phosphate (TBP), kerosene, and many other organics. These organics are sometimes present mixed with radioactive waste, and in these cases it is important to destroy the organics in such a way as to not increase the total volume of the waste and to ensure that no radioactivity is released in the process. Among the most promising techniques for treating aqueous mixed wastes are ultraviolet light (UV) oxidation and the molten salt process, as opposed to methods like incineration or supercritical water oxidation that might lead to air emissions of radioactivity if not very carefully controlled.

The purpose of the present study was to compare the energy efficiency of various commercial UV lamp systems designed for photooxidation. Two type of tests were conducted: 1) direct photolysis of a chlorinated compound and 2) photolysis of hydrogen peroxide, which is an additive often used to photooxidize compounds that are not amenable to direct photolysis. The results should allow LLNL to select the most cost-effective system for treating wastes by UV-enhanced radical oxidation processes.

THEORETICAL

LIGHT SOURCES

The design and photophysics of excimer lamps, pulsed xenon lamps, and conventional mercury arc lamps have been compared recently (Haag, 1994). Continuous mercury arc sources with lifetimes >1000 h and are well established for industrial use. Among the most common and efficient are low pressure mercury lamps, which have almost all their output in a line at 254 nm. The latter lamps also have ~15% of their output at 185 nm if the quartz envelope allows its passage. Despite their high efficiency, the low power density of low pressure mercury lamps makes them impractical for treatment systems, and therefore medium pressure lamps are most commonly used in such applications (Hereaus and PSI Technical Literature). These lamps have most of their emmission in discreet lines above 240 nm, notably at 240, 254, 267, 305, 313, 334 and 366 nm (see Figure 1).

Flashlamps operate in the pulsed mode with peak temperatures and intensities much greater than those occurring with continuous sources of the same average power. Thus, while continuous lamps primarily emit lines associated with the electronic excitation levels of the un-ionized fill gas, pulsed lamps emit light consisting mostly of black body radiation upon which the electronic lines are superimposed (see Figure 1). The xenon pulsed lamp has a broad band output in the range 200 - 300 nm with a peak at 230 nm. Unique features of pulsed lamps include the ability to come to full power immediately (without a warm-up period), and the ability to shift the spectrum of a single lamp simply by changing the peak pulse power.

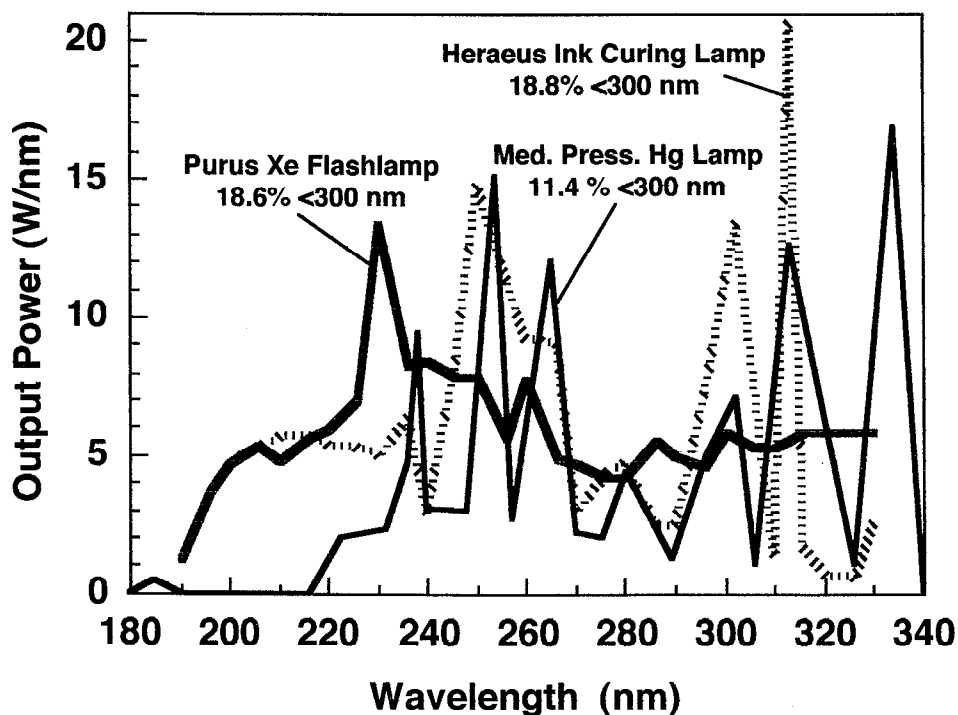


Figure 1. Comparison of lamp spectra as given by manufacturers, normalized to 3675 W. Percentages are given as fraction of electrical input yielding light output below 300 nm.

Excimer lamps are another source of low-wavelength UV light, among the most efficient of which is the 172-nm emission from the excited Xe₂ dimer (Eliasson & Kogelschatz, 1988). These sources, like low-pressure Hg lamps, operate in glow discharge mode, where the fill gas is near room temperature and thus gives emissions associated with specific electronic transitions and almost no broad-band, black-body radiation. Excimer sources for large-scale treatment systems are just now approaching commercial availability. They offer potential benefits of unique lamp geometries and a range of wavelength choices including sub-200 nm wavelengths suitable for direct photolysis of many organic compounds.

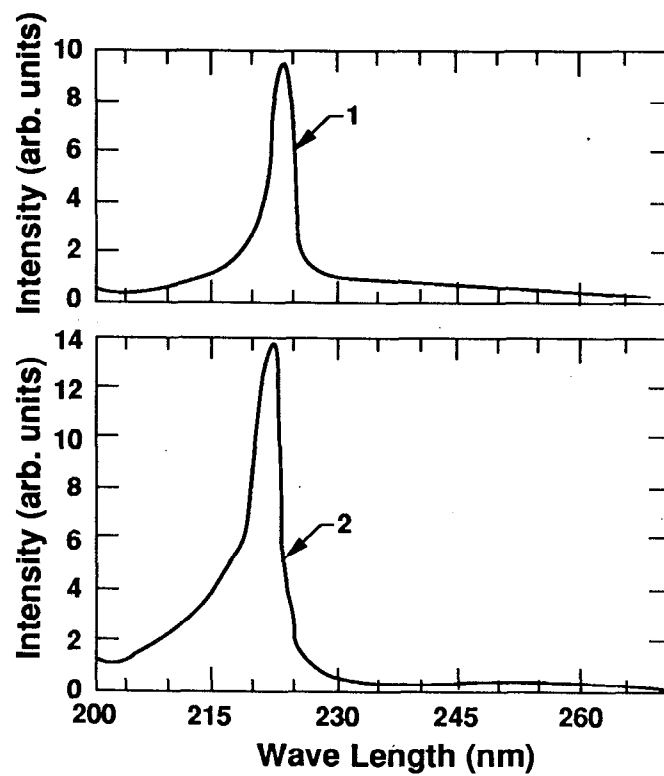


Figure 2. Relative spectra of the KrCl excimer at 6 Torr: a) 3:1 Kr:HCl, b) 3:1 Kr:Cl₂.

The commercial literature gives varying claims for the electrical efficiency of lamps proposed for water treatment. Low-pressure mercury lamps typically have 30 - 60% of the input energy converted to photons below 300 nm, medium-pressure mercury lamps are given at 10 -30% (Hereaus and PSI Technical Literature), and xenon flashlamps 15 - 20% (Haag, 1994). Xe₂ Excimer lamps have inherent efficiencies of 5 - 30% (Eliasson & Kogelschatz, 1988), but practical efficiencies are considerably lower. Competitive light absorption by oxygen and quartz envelopes may limit the usefulness of the 172-nm Xe excimer source in commercial systems. Therefore, it was of interest to study the energy efficiency of a KrCl excimer, which has its peak at 222 nm (Figure 2).

CHEMICAL ACTINOMETRY

The output of light sources of varying geometries can usually be measured more conveniently with a chemical actinometer than with photoelectric detectors. The rate of photolysis of a compound P in a liquid phase reactor can be defined as (Zepp & Cline, 1977):

$$-d[P]/dt = I_0 \Phi \{1 - \exp(-2.303 \epsilon l [P])\} \quad (1)$$

where I_0 is the incoming light intensity (in einsteins L⁻¹ s⁻¹),

Φ is the overall photolysis quantum efficiency (in mol P einstein⁻¹),

ϵ is the decadic molar extinction coefficient of the photolyte P (in L mol⁻¹ cm⁻¹), and

l is the light pathlength (in cm)

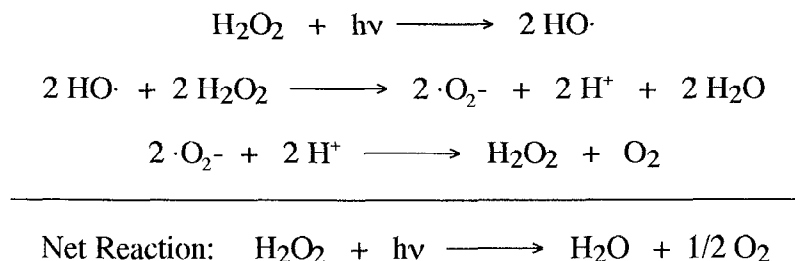
Photolysis of H₂O₂ at high total absorbance

Under high absorbance conditions ($\epsilon l [P] > 1$), essentially all the light in solution is absorbed, and Eq 1 reduces to:

$$-d[P]/dt = I_0 \Phi = k_0 \quad (2)$$

In this case the consumption of photolyte is zero order, and the intensity of the light can be calculated from Eq 2 with knowledge of Φ and the measured k_0 .

In the case where P is hydrogen peroxide, the primary quantum yield is 0.5, and the quantum efficiency Φ for loss of H₂O₂ is 1.0, based on the reactions given below:



This reaction scheme and stoichiometry have been demonstrated by several authors (Hunt & Taube, 1952; Weeks & Matheson, 1956; Baxendale & Wilson). Nicole *et al.* (1990) have reviewed this chemistry and have documented the use of hydrogen peroxide as an actinometer. Because of the coincidence that $\Phi = 1.0$, the zero-order rate of peroxide consumption gives directly the rate of photon emission from the lamp over the wavelength range of complete light absorption.

Eq 1 is actually dependent on wavelength, and therefore under polychromatic light conditions the rate of photolysis should be calculated as the integral over all wavelengths emitted by the lamp and absorbed by the photolyte. Because the extinction coefficient of H_2O_2 decreases at longer wavelengths, the high absorbance approximation no longer holds above a certain wavelength dependent on the concentration used. However, it will be seen that with the lamps used, the amount of photolysis contributed by the long wavelengths, where absorption is partial, is sufficiently small that the zero-order approximation holds adequately for the present purposes.

Photolysis at low total absorbance

At low total absorbance, one can use the approximation $1 - \exp(-x) \approx x$, and Eq 1 reduces to:

$$-d[\text{P}]/dt = 2.303I_0\Phi\epsilon l[\text{P}] = k_1[\text{P}] \quad (3)$$

In this case the consumption of photolyte is first order, and the intensity of the light can be calculated from Eq 3 with knowledge of Φ and the measured k_1 . Alternatively, if Φ is unknown, a relative measure of lamp efficiencies can be made by comparing measured k_1 values directly.

EXPERIMENTAL

Characteristics of the light sources investigated in this study are listed in Table 1.

The PSI system was a donated demonstration unit from 1990. The lamp is driven by an AC current that deviates somewhat from a pure sinusoidal wave, having a delay of low current between the positive and negative waves. The lamp emission spectrum was not supplied by the manufacturer, but is expected to be qualitatively similar to that of the older PSI medium pressure Hg lamp shown in Figure 1 (PSI technical literature).

The Hanovia lamp was chosen because it has characteristics very similar to that of the PSI lamp. The Canrad-Hanovia power supply used to drive it was modified to run with a 480 V transformer.

The Heraeus lamp is a commercial lamp used for ink curing. It was selected because the manufacturer had indicated recent improvements in the transmission of the glass to sub-250 nm

light (Figure 1). The manufacturer indicated that the Canrad-Hanovia power supply was appropriate to drive the lamp.

The Purus pulsed xenon system showed promise because of its high output below 240 nm (Figure 1). It also has the advantage that disposal of used lamps does not involve any hazardous materials, such as Hg or Cl₂ present in the other lamps tested.

The KrCl excimer system was a prototype system used because no commercial systems were available at project initiation. It was operated with 3:1 Kr:Cl₂ fill gas at <100 Torr. This lamp was cooled by water flow in its center axis. The reactor for this lamp consisted of a 2- or 4-L cylinder on a magnetic stirrer. These cylinders gave 0.6 cm and 1.0 cm pathlengths, respectively, between the outer lamp and inner reactor walls. The concentration of H₂O₂ was selected (1600 and 1000 ppm, respectively) to give >90% light absorption below 240 nm.

Table 1. Characteristics of Light Sources used for Photolysis Experiments

Lamp Type	Power Supply	Lamp length x o.d. (cm)	Total Power (kW)	Max. Power (W/cm)
PSI ^a Med. Press. Hg	PSI Demo	25 x 2	2.3	90
Hanovia Med. Press. Hg model 6806A431	Canrad-Hanovia model 55501.221	16 x 2	2.3	140
Heraeus Med. Press. Hg	Canrad-Hanovia model 55501.221	10.6 x 2	1.2	113
Purus Pulsed Xe	Purus LP-701	15 x 5	3.7	250
Russian KrCl Excimer	Russian	43	0.5	12

^a Peroxidation Systems, Inc.

Photooxidations using the xenon and mercury lamps were conducted in a reactor called LP-701, a Purus photooxidation system containing an 17.8-L cylindrical stainless steel vessel 25 cm in diameter and 36 cm in height. Lamps were inserted into a 7-cm diameter cylindrical Suprasil well concentric to the reactor cylinder, leaving an effective light pathlength of 9 cm through the solution. For the Hg lamps, a thin glass tube was inserted into the quartz well to provide a low flow of cooling gas. For the Xe pulsed lamp, deionized water was recirculated through the well in direct contact with the lamp, for cooling. The process water is also recirculated by an external pump, to effect stirring. The volume of liquid in the pump and associated tubing is about 0.7 L, so that

96% of the solution is being exposed in the reactor at any given time. The recirculated process water passes through a heat exchanger to allow cooling with chilled water.

Mercury lamps were given several minutes to warm up before initiating the reaction by injecting about 100 mL of concentrated solution of peroxide or TCAA. To hasten mixing, these photolyte solutions were added through a long-stem funnel that was raised and lowered during the addition process. Mixing was complete in ~1 - 2 minutes, and any early data showing evidence of incomplete mixing were discarded. Because pulsed Xe lamps come to full power immediately, runs with this source were initiated by switching on the lamp after allowing several minutes for mixing.

For peroxide experiments, samples were taken at regular time intervals and residual H_2O_2 determined by Ti^{IV} complexation in dilute sulfuric acid (Satterfield and Bonnel, 1955). The resulting solutions were analyzed by UV absorption at 406 nm in a 1-cm cell on an HP-8453 Diode-array spectrophotometer. Experiments with trichloroacetic acid (TCAA) were conducted by measuring chloride ion formation continuously using an Orion pH/mVmeter fitted with a chloride ion selective electrode. The electrode was inserted into the recirculating process water loop and was calibrated in this position by diluting standard NaCl solutions into the reactor. The latter was done because the high speed of the water caused a shift in the electrode potential compared to stationary standards.

The absorption spectrum of TCAA was measured on the same spectrometer using gravimetrically prepared solutions whose concentrations were verified by titration with standard NaOH.

RESULTS AND DISCUSSION

H_2O_2 actinometry was chosen to measure lamp efficiency because of its simplicity and ease of comparison with previous data obtained with the pulsed Xe lamp in the same reactor (Haag, 1994). Use of high concentrations of H_2O_2 allowed measurement of the overall efficiency of the lamps. From the H_2O_2 absorption spectrum (Figure 3; Schumb, *et al.*, 1955), it was calculated that the initial concentrations of about 2000 ppm (0.06 M) resulted in >90% light harvesting below 300 nm. Figure 4 shows sample plots demonstrating that under these conditions the loss of peroxide followed the expected zero-order kinetics.

TCAA was chosen as a model compound undergoing direct photolysis of carbon-chlorine bonds. It was used at low concentration (100 μM) where most of the light was transmitted through the solution and lost to the reactor walls (maximum initial absorbance of 0.4). Figure 5 is an example showing that the formation of chloride ion is first order. Reactions subsequent to the

initial chlorine-carbon bond photolysis are expected to release the other two chlorine as well, and this assumption is verified by the approximate 3:1 ratio of chloride formed to TCAA added.

Table 1 summarizes all the H_2O_2 actinometry results. Interestingly, all the lamps except the KrCl excimer gave close to the same efficiency. The PSI lamp data show that the output is independent of cooling air flow rate until a high value (>5 L/min.) is reached, whereupon the lamp is too cool to allow complete vaporization of the mercury, and the emission drops dramatically. The same effect is observed with the Hereaus lamp at 0.50 kW, where the low power prevents the lamp from self-heating to a high enough temperature even without air cooling. Therefore these data were omitted from the calculation of average efficiencies. Another point discarded was the anomalously high value for the 3 L/min. PSI run, which was the very first experiment and could not be reproduced.

The peroxide results for the Purus pulsed Xe lamp were in agreement with the numerous measurements made previously with the same reactor - lamp system (Haag, 1994). These data averaged 46 ± 3 g $\text{H}_2\text{O}_2 \cdot \text{kWh}^{-1}$ when normalized to the lamp current draw of 3.7 kW. The present measurements indicate that the power supply requires about 5.1 kW to drive the 3.7 kW lamp, or about 72% current efficiency. Accounting for this efficiency yields $0.72 \times 46 = 33$ g $\text{H}_2\text{O}_2 \cdot \text{kWh}^{-1}$ of wall power, in exact agreement with the present results. The manufacturer (Bart Mass, personal comm 1996) indicated that the supply system was not optimized and a significantly higher efficiency could be achieved. However, we chose to use the actual measured power consumption for normalization because similar claims might also be made for the other power supplies.

The poor efficiency of the KrCl excimer lamps reflected its difficulty of operation. The lamp continually lost fill gas pressure due to reaction and possibly leaks. It was necessary to continually replenish the fill gas to maintain a discharge, resulting in periods of weak emission with nearly the same power consumption. In addition, the electrode corroded, causing some deposition of metal on the quartz wall and explaining the drop in efficiency between the first and second run. It should be emphasized that this lamp was a prototype and was used because no commercial systems were available at the time the study was started. Subsequently, much higher quality and power excimer lamps have become available (Hereaus technical literature), and we do not believe that the current poor performance is representative of efficiencies that can now be achieved commercially.

The results in Table 2 for TCAA photolysis show that, once again, all lamps had nearly the same efficiency. Because these experiments emphasized the wavelengths below 250 nm, it is seen that the output of all of these lamps must be similar in this region. This result indicates that the PSI and Hanovia lamps must have more low-wavelength output than the earlier PSI medium pressure lamp whose spectrum is given in Figure 1.

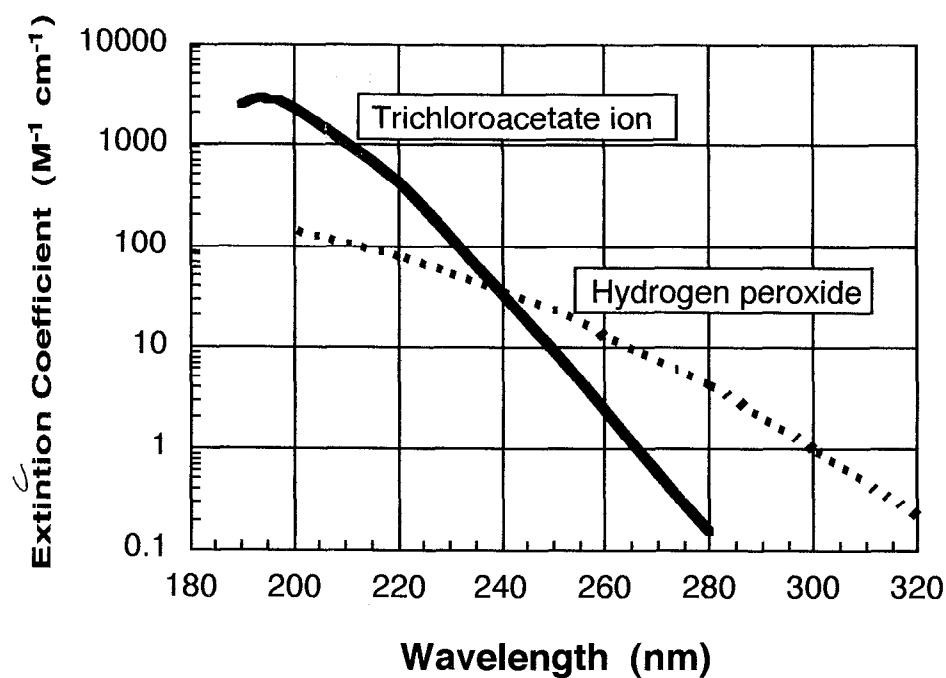


Figure 3. Aqueous absorption spectra of H_2O_2 (Schumb *et al.*, 1955) and trichloroacetate ion. TCAA data from 0.1 and 1 mM ($\text{pH} \geq 3$) solution where all TCAA should be ionized ($\text{pK}_a = 0.7$).

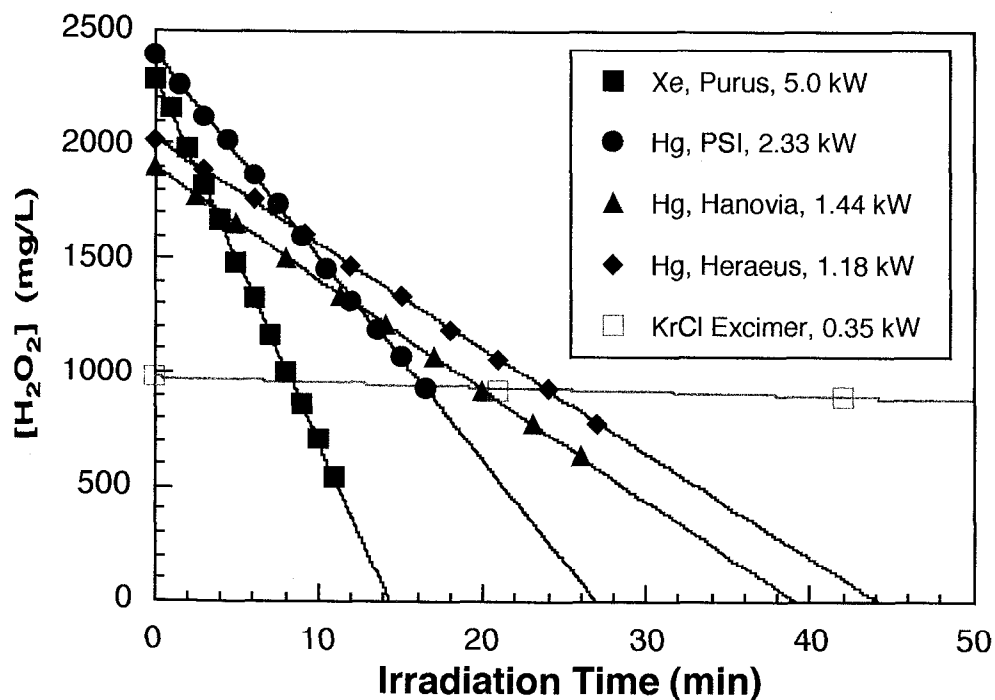


Figure 4. Examples of hydrogen peroxide photolyses demonstrating zero order kinetics. All photolyses were conducted at $30 \pm 5^\circ\text{C}$ in the 18-L LP-701 reactor except for the KrCl excimer lamp run, which used the 2-L graduated cylinder.

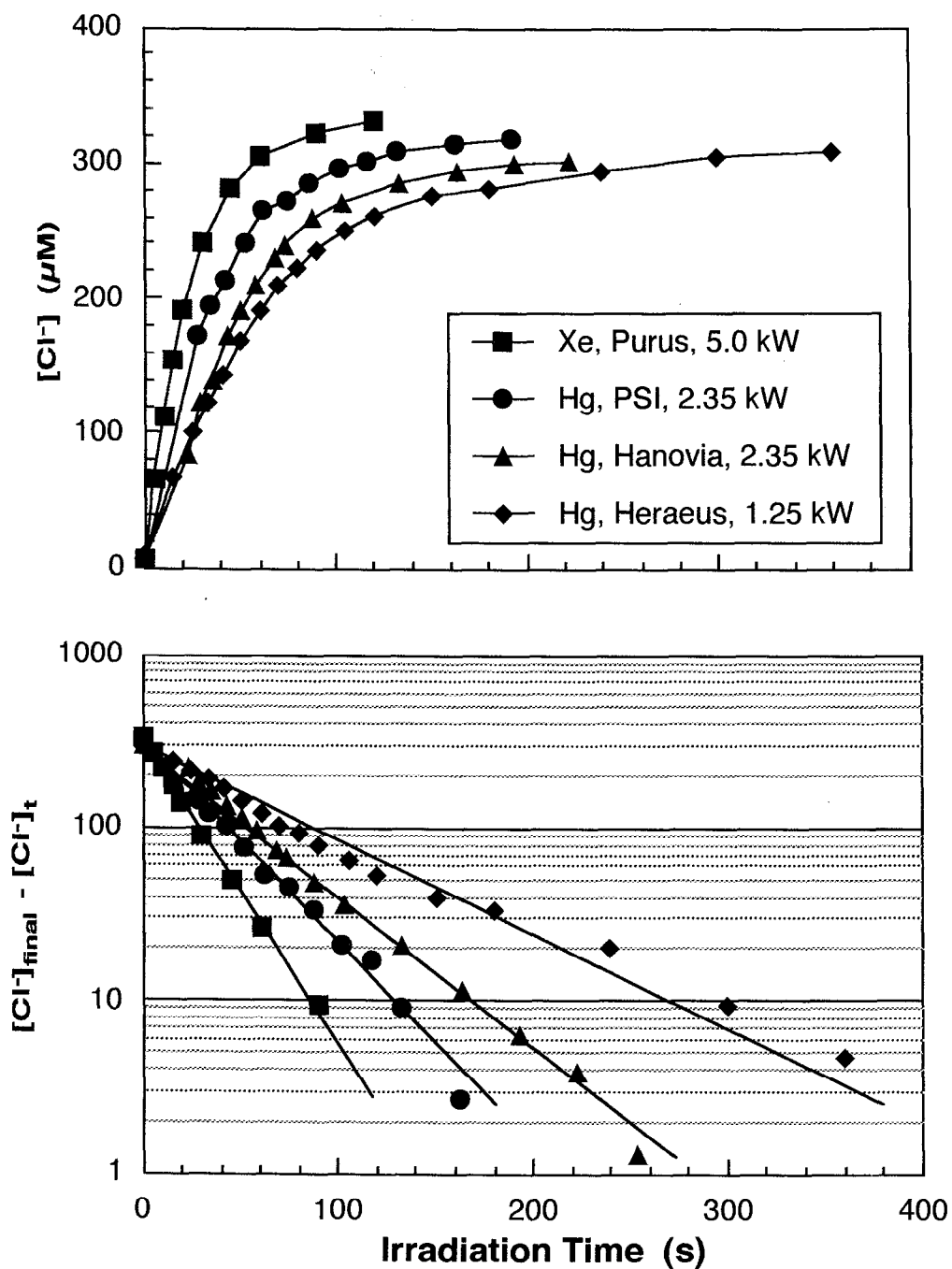


Figure 5. Formation of chloride during the photolysis of TCAA in LP-701. The data in the lower graph are from the same experiments as in the top, but replotted show first-order kinetics

Table 1. Summary of H₂O₂ Photolysis Experiments

Lamp	Reactor Vol. (L)	Power (kW)	Lamp Cooling Fluid Flow (L/min)	Water Temp. (°C)	Photolysis Rate (mg·L ⁻¹ ·min ⁻¹)	Efficiency (g H ₂ O ₂ · kWh ⁻¹)	Efficiency (E·MJ ⁻¹)*
Purus Xe	17.8	5.0	water	27	159	34.0	0.28
Purus Xe	17.8	5.3	water	24	158	31.9	0.26
Purus Avg:						33.0	0.27
PSI #1	17.8	2.3	none	32	84	39.0	0.32
PSI #1	17.8	2.3	none	33	88	40.9	0.33
PSI #1	17.8	2.31	none	27	72	33.3	0.27
PSI #1	17.8	2.33	2 (N ₂)	34	89	41.3	0.34
PSI #1	17.8	2.3	2 (air)	32	96	44.6	0.36
PSI #1	17.8	2.3	3 (air)	32	173	80.3	0.66
PSI #1	17.8	2.3	5 (air)	33	82	38.1	0.31
PSI #1	17.8	<<2.3	>10 (air)	25	7.8	> 4	≥0.029
PSI #2	17.8	2.31	2 (air)	32	79	36.5	0.30
PSI #2	17.8	2.33	2 (air)	30	70	32.1	0.26
PSI Avg:						38.2	0.31
Hanovia	17.8	0.84	none	30	32	40.7	0.33
Hanovia	17.8	1.44	none	31	48	35.8	0.29
Hanovia	17.8	2.33	none	37	81	37.3	0.30
Hanovia Avg:						37.9	0.31
Hereaus	17.8	0.50	none	28	13.8	29.6	0.24
Hereaus	17.8	1.22	none	31	44	38.3	0.31
Hereaus	17.8	1.18	none	25	46	41.3	0.34
Hereaus	17.8	1.22	2 (air)	29	48	41.8	0.34
Hereaus Avg:						40.5	0.33
KrCl	0.85	0.54	water	35	12.7	1.7†	0.014
KrCl	1.77	0.35	water	25	1.9	1.1†	0.009
KrCl Avg:						1.4	0.012

* E·MJ⁻¹ = Einsteins per megajoule.

† These runs also normalized for differing fractions of lamp length immersed in solution.

Table 2. Summary of TCAA Photolysis Experiments

Lamp	Power (kW)	Lamp Cooling Fluid Flow (L/min)	T (°C)	k_1 (s ⁻¹)	k_1 (MJ ⁻¹) *
Purus Xe	5.0	water	24	0.0344	6.9
Purus Xe	5.0	water	19	0.0408	8.2
Purus Xe	5.0	water	24	0.0413	8.3
PSI #2	2.35	2 (air)	27	0.0265	11.3
PSI #2	2.35	2 (air)	26	0.0230	9.8
Hanovia	2.38	2 (air)	31	0.0193	8.1
Hanovia	2.30	2 (air)	27	0.0273	11.9
Hanovia	2.35	2 (air)	27	0.0413	8.3
Hanovia	0.48	2 (air)	22	0.0011	2.4
Hereaus	1.25	2 (air)	23	0.0127	10.2
Hereaus	1.25	2 (air)	26	0.0143	11.4

* MJ = megajoule; this energy-normalized rate constant equals k_1 in s⁻¹ divided by power consumption on megawatts.

CONCLUSIONS

The Purus pulsed Xe lamp systems have about the same energy efficiency as commercially available medium pressure Hg lamp systems. The greater complexity (higher capital cost) and shorter demonstrated life of the pulsed lamps are obstacles to their implementation for LLNL waste oxidation. Advantages include the ability to come to power immediately, and the absence of mercury, which becomes a hazardous waste itself. The KrCl excimer studied had too low an efficiency to be considered a viable alternative, but it is premature to extend this conclusion to all excimer lamps before newer commercially available excimer systems are tested.

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